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Author: M. Mazurek, Agata Lisińska-Czekaj, Z. Surowiec, E. Jartych, Dionizy Czekaj

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Structure and Hyperfine Interactions in Aurivillius $Bi_9Ti_3Fe_5O_{27}$ Conventionally Sintered Compound

M. Mazurek[a,*], A. Lisińska-Czekaj[b], Z. Surowiec[c], E. Jartych[a] and D. Czekaj[b]

[a]Department of Experimental Physics, Institute of Physics, Technical University of Lublin Nadbystrzycka 38, 20-618 Lublin, Poland

[b]Department of Materials Science, University of Silesia, Śnieżna 2, 41-200 Sosnowiec, Poland

[c]Institute of Physics, Maria Curie-Skłodowska University, pl. M.C. Skłodowskiej 1, 20-031 Lublin, Poland

The structure and hyperfine interactions in the $Bi_9Ti_3Fe_5O_{27}$ Aurivillius compound were studied using X-ray diffraction and Mössbauer spectroscopy. Samples were prepared by the conventional solid-state sintering method at various temperatures. An X-ray diffraction analysis proved that the sintered compounds formed single phases at temperature above 993 K. Mössbauer measurements have been carried out at room and liquid nitrogen temperatures. Room-temperature Mössbauer spectrum of the $Bi_9Ti_3Fe_5O_{27}$ compound confirmed its paramagnetic properties. However, low temperature measurements revealed the additional paramagnetic phase besides the antiferromagnetic one.

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1. Introduction

Recently, an upsurge of scientific interest in multiferroic materials may be observed. In multiferroics ferroelectric and ferro(antiferro-)magnetic (and/or ferroelastic) properties are simultaneously combined and these are materials known from 1960s ([1] and Refs. therein). Until now, however, the microscopic mechanism of coexistence in one material the magnetic and ferroelectric ordering is not well recognized, especially in systems with perovskite-like structure ($BiFeO_3$, $BiMnO_3$, $YMnO_3$) or in Aurivillius compounds [1, 2].

The Aurivillius compounds of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system are described with the general formula $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ where m indicates the number of perovskite-like layers $\{(Bi_{m+1}Fe_{m-3}Ti_3O_{3m+1})^{2-}\}$ per slab between fluorite-like bismuth-oxygen layers $\{(Bi_2O_2)^{2+}\}$. These compounds are ceramics which combine ferroelectric, semiconducting and antiferromagnetic properties making them very attractive materials to applications in information processing and storage ([3] and Refs. therein). In this work the investigated $Bi_9Ti_3Fe_5O_{27}$ compound has eight perovskite layers between the Bi_2O_2 layers.

The traditional solid-state sintering technology for preparation of ceramic materials is widely used and well established. While the structure of the Aurivillius compounds is described in the literature and databases quite well, the hyperfine interactions in these materials have not yet been studied in sufficient detail. In our earlier papers [4, 5] room-temperature Mössbauer measurements performed for $Bi_{m+1}Ti_3Fe_{m-3}O_{3m+3}$ with $m = 4, 6, 7$ and 8 revealed that all compounds were in paramagnetic state, what is consistent with the literature data concerning the Néel temperature of these ceramics (T_N is smaller than room temperature) [6]. Low temperature Mössbauer measurements for $Bi_9Ti_3Fe_5O_{27}$ compound have been carried out more than thirty years ago [7, 8], however, besides spectra not all values of hyperfine interaction parameters were reported by the authors.

The aim of this work was to determine the hyperfine interaction parameters of $Bi_9Ti_3Fe_5O_{27}$ compound both at room and liquid nitrogen temperatures using Mössbauer spectroscopy (MS). Structure of the sintered $Bi_9Ti_3Fe_5O_{27}$ ceramic was investigated using X-ray diffraction (XRD).

2. Experimental details

To prepare the $Bi_9Ti_3Fe_5O_{27}$ compound the appropriate amounts of precursors, viz. Fe_2O_3, Bi_2O_3, and TiO_2 (all 99.9% purity, Aldrich Chemical Co.) were weighted and mixed with an agate mortar and pestle to give the desired composition and thus provide conditions for the following solid state reaction:

$$6TiO_2 + 9Bi_2O_3 + 5Fe_2O_3 \rightarrow 2Bi_9Ti_3Fe_5O_{27}. \quad (1)$$

The mixture of powders was pressed under 300 MPa in 20 mm diameter stainless-steel die. The obtained compacts were then placed in an alumina crucible and fired

* corresponding author; e-mail: mariusz.mazurek@pollub.pl

in air at temperature 993 K for 2 hours. As EDS (Energy Dispersive Spectroscopy) measurements performed after calcination proved, the chemical composition of the compound was conserved with the relative accuracy of ±3%. After calcination the compacts were re-milled, pressed into discs of 10 mm in diameter under 600 MPa, and then sintered at temperatures 1123 K and 1223 K, for 2 h in a sealed alumina crucible (free sintering method), with heating and cooling rates of 5 K min^{-1}. All the samples were then furnace-cooled to room temperature.

XRD measurements were performed using the Philips PW3710 diffractometer with CoK_α radiation. The analysis of X-ray patterns was performed with an X'Pert HighScore Plus computer programme equipped with the newest ICSD data base and Rietveld method of the crystalline structure refinement.

MS studies were carried out at room and liquid nitrogen temperatures in standard transmission geometry using a source of ^{57}Co in a rhodium or a chromium matrix.

3. Results and discussion

As reported in our earlier work [5], X-ray diffraction and Mössbauer studies revealed that the $Bi_9Ti_3Fe_5O_{27}$ compound synthesized at 993 K contained residual hematite. Sintering at 1123 K and 1223 K resulted in the formation of the single-phased compound. A detailed analysis of XRD measurements allowed to determine the lattice parameters for the $Bi_9Ti_3Fe_5O_{27}$ compound which are as follows: $a = 5.602(4)$ Å, $b = 5.536(5)$ Å, $c = 75.16(5)$ Å, $\alpha = \beta = \gamma = 90°$ and agree well with the data reported in [3].

Figure 1 presents room-temperature Mössbauer spectrum obtained for the $Bi_9Ti_3Fe_5O_{27}$ compound sintered at 1123 K. In order to reveal some details of the Mössbauer spectrum it was registered at smaller velocity range. For the sample sintered at 1223 K both XRD and MS studies gave the similar results.

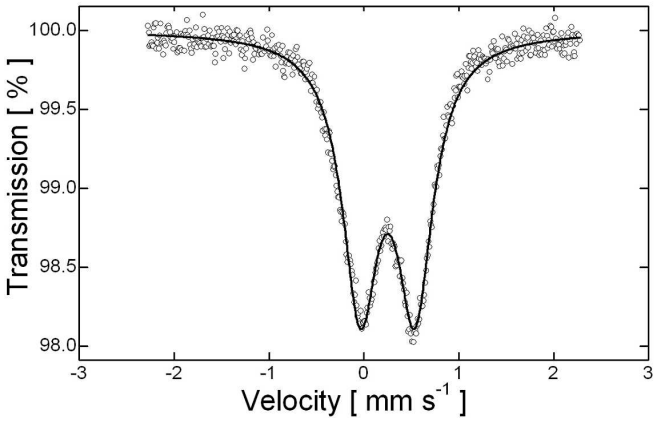

Fig. 1. Room-temperature Mössbauer spectrum of $Bi_9Ti_3Fe_5O_{27}$ compound sintered at 1123 K.

In the numerical fitting procedure the spectrum was fitted using one doublet what reflects one ^{57}Fe-position, i.e. in the center of the oxygen octahedron, where iron may substitute Ti atoms. The hyperfine interaction parameters are listed in Table and they are typical for the high spin trivalent iron.

It is known that the Aurivillius compounds are antiferromagnetics and with increasing the number of perovskite-like layers, the antiferromagnetic Néel temperature increases ([6] and Refs. therein) being smaller than room temperature for $m = 4$–7. In the case of the $Bi_9Ti_3Fe_5O_{27}$ compound there are some discrepancies in the reported data. The value of T_N is estimated as greater than 300 K by the authors of [9]. Our results agree well with the data reported in [7], where the authors have observed the quadrupole doublets at 270 K and 300 K. Moreover, they have suggested that in the $Bi_9Ti_3Fe_5O_{27}$ compound the Néel temperature had no precisely determined value but the transition from antiferromagnetic to paramagnetic state may occur at various temperatures from a relatively broad range, i.e. between 80 K and 270 K.

In Fig. 2 Mössbauer spectrum measured for the $Bi_9Ti_3Fe_5O_{27}$ compound at liquid nitrogen temperature (80 K) is shown. It may be seen, that besides the six-line pattern the doublet line exists in the spectrum. This means that some second phase, invisible in XRD pattern as well as in room temperature MS spectra, exists in the sample. Qualitatively, our spectrum is similar to that reported in [7, 8] where the authors have observed the spectra consisted of doublet and sextets at temperature range of 80–270 K. However, at 80 K they have registered broadened six-line pattern without a doublet [7].

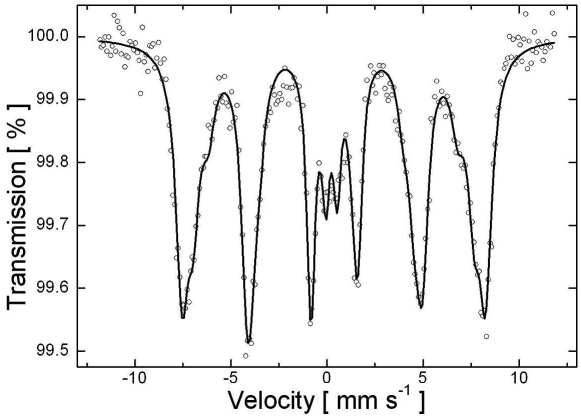

Fig. 2. Liquid nitrogen temperature Mössbauer spectrum of $Bi_9Ti_3Fe_5O_{27}$compound.

The numerical fitting of the spectrum was performed using one doublet and three sextets with no fixed parameters. The hyperfine interaction parameters of the components are listed in Table.

TABLE

Hyperfine interaction parameters obtained from the numerical fitting of the Mössbauer spectra for $Bi_9Ti_3Fe_5O_{27}$ compound measured in room temperature (RT) and liquid nitrogen temperature (LN): δ — isomer shift relative to α-iron, QS — quadrupole splitting of the doublet, Δ — quadrupole shift of the magnetically split spectrum, B_{hf} — hyperfine magnetic field, Γ — half width at half maximum of spectral lines, $C1 : C2 : C3$ — ratio of line amplitudes in sextets; uncertainty of the parameters are given in parentheses for the last significant numbers.

	δ [mm/s]	QS [mm/s]	Δ [mm/s]	B_{hf} [T]	Γ [mm/s]	$C1 : C2 : C3$	χ^2	Remarks
RT	0.35(1)	0.28(1)	—	—	0.23(1)	—	1.01	doublet
LN	0.32(1)	0.29(1)	—	—	0.25(2)	—	0.98	doublet
	0.37(3)	—	−0.03(2)	40.38(28)	0.35(5)	2.5 : 2 :1		sextet 1
	0.42(1)	—	−0.02(1)	45.49(19)				sextet 2
	0.46(1)	—	0.02(1)	49.18(10)				sextet 3

4. Conclusions

On the basis of the performed X-ray diffraction studies it may be stated that Aurivillius compound $Bi_9Ti_3Fe_5O_{27}$ prepared by sintering is a single-phased material. However, Mössbauer spectroscopy revealed the existing of the second phase and distribution of hyperfine magnetic field.

The second phase, which has practically the same hyperfine interaction parameters as the major one, may originate from the isolated iron-oxygen octahedra of the almost the same symmetry as the main $Bi_9Ti_3Fe_5O_{27}$ compound. Three sextets, giving some kind of distribution, may be caused by some non-collinear magnetic structure.

The main result of this work is the determination of the value of hyperfine magnetic field induction which was done firstly, in accordance with the knowledge of the authors.

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